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(54) Title: MELTPROCESSIBLE STARCH COMPOSITION, A PROCESS FOR THE PREPARATION THEREOF AND THE USE OF THE COMPOSITION			
(57) Abstract			
<p>The invention concerns a biodegradable starch composition, a process for the preparation thereof, the use of the composition and a process for increasing the degradation rate of intermediate products manufactured from starch derivatives and/or products made therefrom under conditions of biodegradation. According to the invention the composition contains 5 to 99 wt-% of a plasticized starch derivative and 1 to 95 wt-% of a biodegradable fibrous material. The microstructure of the composition is discontinuous and formed by a phase containing the starch derivative and a phase containing the fibrous material and any porosity, and its impact strength is at least 10 % better than the corresponding values of a plasticized starch derivative. The composition may further contain 0.01 to 30 wt-% of a biodegradable polyester, such as polylactide, polycaprolactone or a cellulose ester. According to the invention, the biodegradable starch composition is prepared by esterification of starch with glycerol in order to form a mixture containing starch acetate and acetic acid and then the mixture is blended with a biodegradable fibrous material for producing a composition which has a discontinuous microstructure. The invention provides a melt processible composition having good water resistance and mechanical properties which can be regulated by changing the relative amounts and the qualities of the components of the composition.</p>			

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Meltprocessable Starch Composition, a Process for the Preparation Thereof and the Use of the Composition

5 The present invention relates to a melt-processible starch composition according to the preamble of claim 1. Such a composition crumbles in the compost.

10 The invention also relates to a process for the preparation of a starch composition that crumbles in the compost. According to said method a native starch is esterized in order to produce the plasticized starch derivative.

15 Environmental concerns and green concepts are creating new markets for products based on renewable resources. These trends are seen e.g. in the industrial sectors of packaging, hygiene and glue, for which recyclability, reusability, compostability, biodegradability and nonstressability of the environment are contemporary requirements. There is also an increasing trend to substitute petrochemically derived products with refined biopolymers.

20 Thermoplastization of natural polymers, in particular starch, is discussed in a large number of patents and patent applications (e.g. GB 2 190 093 A, US 4 673 438, EP 282 451 A3, EP 0 298 920 A3, EP 0 304 401 A2, EP 0 326 517 A1), which disclose opening of the granular structure of starch by melt processing generally in the presence of water and some plasticizer such as glycerol, ethylene glycol and oligomers thereof, and other adjuvants. Even if the products thus obtained are thermoplastic and biodegradable, their water resistance is poor which considerably limits their use. These kinds of thermoplastic starch products tend to absorb water when the humidity of air is high, which changes their mechanical properties. On the other hand, at low moisture contents, the water contained in the product evaporates and the products become more brittle.

25 Attempts have been made to improve the properties (water resistance and mechanical properties) of thermoplastic starches by blending them with synthetic polymers, as disclosed, e.g., in the following applications: EP 0 404 723 A2, EP 0 409 788 A3, EP 0

404 727 A3, EP 0 404 728 A3, EP 0 408 501 A3, EP 0 408 502 A3, EP 0 409 782 A3 and EP 0 409 781 A3, FI 902662, WO 92/19680, FI 921264 and EP 0 519 367 A1.

Often the used synthetic polymers are hydrophilic and even if they do improve the mechanical properties the water resistance of the products still remains poor. The above-mentioned patent application describe improvement of the water resistance of thermoplastic starches by blending them with traditional thermoplastic polymers, poly-olefins and polyesters, prepared from the raw materials of petrochemistry. The thus obtained blends and mixtures are heterophasic and their biodegradability is lowered due to the increased amounts of non-degradable components.

10

Starch has been mixed also with biodegradable synthetic polymers in addition to synthetic, nondegradable polymers (e.g. poly(caprolactone), polylactide), as has been described in the following patent applications and articles: WO 92/19680, EP 0 530 987 A1, EP 0 535 994 A1, Koenig, M.F. and Huang, S.J., Biodegradable Polymers / Starch Blends, Composites and Coatings, Polymer Materials Science Engineering 67(1992) s. 290-291. Starch has increased the biodegradability of the mixture, but essentially diminished the mechanical properties of the blends.

20

Known mixtures of natural polymer derivatives and starch/thermoplasticized starch are blends based on cellulose esters (acetate, propionate and butyrate and mixed esters thereof), described in US patent publications 5 280 055 and 5 288 318. In both patents starch is essentially unmodified. US patent 5 288 318 concerns blends and injection moulded pieces, prepared from cellulose acetate having a defined molar mass (28 000 - 62 000 Dalton), viscosity (3 - 44 s) and acetyl content (34 - 42 %), and unmodified starch, part of which may be granular. The share of cellulose acetate in the blend is 30 - 70 %, starch 10 - 60 % and plasticizer 5 - 35 %. A part of the cellulose acetate can be substituted with acetate prepared from waste paper, whole grain flour or starch. Cellulose acetate improves the water resistance of the hydrophilic, unmodified starch. In US patent publication 5 280 055 starch acetate has been used as compatibilizer to improve the blending of thermoplastic starch and cellulose ester. Cellulose ester improves the water resistance of the thermoplastic starch, but the mechanical properties

diminish (tensile strength 25 --> ca 2 N/mm²) as the share of starch the cellulose acetate butyrate mixture increases (20 % --> 70 %).

In the majority of the investigations above, the starch component is natural starch or 5 starch modified in such a way that it can be plasticized in the presence of water and other hydrophilic plasticizers, or be used in granular form. A more hydrophobic mixture has been attempted through the blending components.

10 The following patents or patent publications concern starch derivatives and compositions prepared thereof. Largely, the modifications have been prepared from special starch, rich in amylose. Synthetic polymers based on petrochemical products have been used to control the properties.

15 US patent publication 3 553 196 and EP patent application 0 546 538 A1 describe the preparation of water soluble casting films from starch acetates having a low degree of substitution, prepared from starch rich in amylose. The usage of the materials is restricted by their water solubility.

20 In the method according to the application WO 92/16583 a biodegradable composition is described, which is produced by melt processing of a starch derivative, an ester or ether, a small amount of plasticizer (water) and alkenol homo- or copolymer (poly(vinyl alcohol)). The fraction of the alkenol polymer in the mixture is 10 - 200 parts to 100 parts of starch. The material has been used to produce candle covers by injection moulding and foamed products for packaging applications. The most suitable degree of 25 substitution of the starch derivatives is > 0.8, for acetates preferably 0.8 - 1.5. No information has been given on the mechanical properties of the mixtures. The alkenol polymer used in the composition is based on petrochemical products, not on renewable resources. Its biodegradability is questionable.

30 Thermoplastic starch products have been produced also by plasticizing starch acetate with suitable plasticizers. The patent application WO 92/19675 describes a starch acyl

derivative, especially acetate, produced from an amylose rich starch, and gelling thereof with biodegradable plasticizers, such as citric acid ethylene esters, glycerol acetates and lactic acid esters. The product has been described as humidity proof, thermoplastic, environmental friendly, translucent and processable to casting films. Good results can be 5 achieved only with products rich in amylose, however, which constrains the choice of starch suitable as raw material.

From the patent application WO 93/20110 a degradable polymer composition is known, which can be processed with heat and pressure into products of high dimensional stability. The composition consists of a starch, which has been esterized from starch rich in 10 amylose (minimum 50 %), and which owns a degree of substitution of at least 1.5 and which is plasticized with softeners (citrates, glyceric esters, phthalate, phosphates, succinates etc.) having molar masses of less than 2,000 g/mol, preferably in the range of 100 to 1,000 g/mol.

15 Fibre reinforced biodegradable materials with natural polymers as filling agents, primarily co- or homopolymers of glycolic acid, have been presented in the EP application 0 533 314. The application describes that the filling agents improve the physical and thermic properties of the biodegradable polymer. No mentioning of starch 20 can be found in said publication.

Biodegradable natural polymer compositions have been presented also in the EP-application publication 0 393 825 and the US patent publication 5 306 550. These publications describe water absorbent, biodegradable polymer compositions, consisting 25 of cellulose fibres, chitosane and gelatinized starch or thermoplastics. The compositions can be processed into films. The products are characterized by that they are water soluble and prepared from a water solution or dispersion. The desired form of the film can be obtained as the water is evaporated.

30 As a summary of the state of the technique, it can be concluded that no known solution has resulted in melt processible starch based polymer compositions, having good

mechanical properties, that would consist only or at least substantially of materials derived from renewable raw material of low cost, and that are easily biodegradable.

5 It is an aim of the present invention to eliminate the problems relating to the prior art and to provide an entirely new melt processible, compostable starch composition, with excellent strength properties. It is also an aim of the invention to provide a novel method for the preparation of the starch composition and a method for enhancing the biodegradability of starch based compositions.

10 The invention is based on the idea that a composition is formed, which contains plasticized starch derivative and a biodegradable fibre agent, and which has a discontinuous micro structure. The composition contains typically ca 5 to ca 99 weight % plasticized starch derivative, which forms the starch derivative phase, and ca 1 to ca 15 95 weight % fibre agent, which forms the fibre agent phase. The latter contributes discontinuous interfaces to the starch component, which enhance the hydrolytic decomposition of the composition.

20 Such a composition is characterized by that its impact strength is at least 10 % better than the values corresponding to a plasticized starch derivative. At the same time the composition decomposes very quickly in a biologic environment, for instance in contact with micro-organisms living in the soil.

25 More specifically, the composition according to the invention is characterized by what is stated in the characterizing part of claim 1.

30 Polymer products, such as boards and films, can be manufactured from the new compositions with methods known per se in polymer technology. The use of the compositions according to the invention is characterized by what is stated in claims 27 - 34.

Furthermore, the invention gives a new method for the production of a compostable starch composition. The method is characterized by that starch is esterized with an acetylating agent together with plasticizers containing OH-groups, such as glycerol, to produce a mixture, which contains starch acetate and an acetylated plasticizer, such as 5 acetic glycerol esters. This mixture can further be blended with a biodegradable fibre agent to produce a composition having a discontinuous micro structure.

10 Optionally, cellulose pulp can be added to the mixture that is esterized, in addition to starch, esterizing agent and plasticizer, such as glycerol. In this case the reaction results in a plasticized blend, which contains cellulose ester in addition to starch ester and acetic glycerol ester.

15 More precisely the method according to the invention is characterized by what is stated in the characterizing part of claims 31 and 36 respectively.

20 The invention provides also a method for enhancing the crumbling of intermediate products and/or products of starch derivatives in biodegrading circumstances such as in a compost. This solution is characterized by that discontinuous interfaces enhancing water adsorption are introduced into the internal structure of the material by mixing biodegradable fibres into the material at latest during the manufacturing of the intermediate product or product.

25 The process for enhancing the crumbling of products manufactured of starch derivatives is characterized by what is stated in the characterizing part of claim 39.

30 Substantial benefits are attained by the invention. The raw materials of the starch composition according to the invention are primarily based on renewable resources and they are biodegradable/compostable. The starch component can be derived from any natural starch; it does not have to be starch rich in amylose. The composition is melt-processible with ordinary plastic processing equipment. It has good mechanical and water resistance properties, which are controllable by changing the shares and qualities

of the components of the composition. The impact strength values of the compositions according to the invention are, in comparison to material that contains no fibre agent, at least 10 %, preferably 50 % and most preferably even more than 100 % better.

5 The material fulfills also the requirements for food packaging by migration simulation tests, and is applicable to injection moulding, films, deep drawing, and to paper and cardboard coating.

Follows a more detailed description of the present invention, together with examples of 10 applications.

According to a preferred form of application of the invention the composition contains ca 30 - 95 wt-% plasticized starch derivative and 5 - 70 wt-% biodegradable fibre agent. When the composition contains 50 wt-% or more plasticized starch derivative, this forms 15 the continuous phase of the composition, in which the fibre agent phase forms discontinuous interfaces, which enhance the biodegradability of the composition.

The "plasticized starch component" means a product, which can be produced from native starch and which can be moulded at a moderate temperature, typically between room 20 temperature and 200 °C, preferably at ca 30 - 180 °C. The starch component can be plasticized by introducing a plasticizing agent, in the presence of which the starch component typically dissolves and swells, or the plasticization can occur as a result of the plasticizing effect of the groups that are chemically bonded to the starch component. The former method can be called external plasticization, and it is applied, e.g., in the 25 case of starch esters. The latter method can be called internal plasticization, and it is used, e.g., in the case of hydroxy alkyl derivatives of starch. The amounts of plasticized starch derivatives given above (5 - 99 % of the weight of the composition) comprise both the starch component and the amount of plasticizing agent, if such is used.

30 A composition containing plasticized native starch together with natural fibres is known from the WO application publication WO 95/04106. In connection with the present

invention it has been noticed, however, that using starch derivatives instead of native starch as starch component, results in compositions having considerably higher impact strength and showing even three times higher water resistance than compositions produced from native starch. In spite of their excellent mechanical properties the 5 compositions according to the invention are also compostable, however.

The plasticized starch derivative of the composition according to the invention, in the following called also the starch component, can be based on any natural starch having an 10 amylose concentration of 0 to 100 % and an amylopectine concentration of 100 to 0 %. Thus, the starch component can be derived from barley, potato, wheat, oat, peas, maize, tapioca, sago, rice and similar bulb or cereal plants. It can be based also on starch derivatives prepared from said natural starch by oxidation, hydrolyzation, cross-linking, cationization, grafting, etherification or esterification.

15 It has been found preferable to use a starch-based component which is derived from an ester formed by starch and one or several aliphatic C₁₋₁₄-carboxylic acids. The carboxylic acid component of an ester of this kind can then be derived from a lower alkane acid, such as acetic acid, propionic acid or butyric acid or a mixture thereof. The carboxylic acid component can, however, also be derived from natural saturated or unsaturated fatty acids. Palmitinic acid, stearic acid and mixtures thereof are examples of the fatty acids. 20 The ester can also comprise both long and short chained carboxylic acid components. The mixed esters of acetate and stearate are examples of the latter esters.

25 The preparation of fatty acid esters of starch can be carried out for example as disclosed in the prior art publication by Wolff,I.A., Olds, D.W. and Hilbert.G.E., The acylation of Corn Starch, Amylose and Amylopectin, J.Amer.Chem.Soc. 73 (1952) 346-349 or Gros,A.T. and Feuge,R.O., Properties of Fatty Acid Esters of Amylose, J.Amer.Oil Chemists's Soc 39 (1962) 19-24.

30 Starch acetated can be prepared by reacting starch with acetic anhydride in the presence

of a catalyst. The catalyst used comprises, for example, 50 % sodium hydroxide. Other preparation processes known in the art for preparation acetates are suitable for preparing starch acetate. By varying the amount of acetic anhydride, the amount of the alkali used as a catalyst, and the reaction time, it is possible to prepare starch acetates having 5 different amounts of degrees of substitution. Barley starch is the model starch used in the examples; the same method is suitable also for other starches (for other natural starches, hydrolyzed starches, oxidized starch, etherified starch etc.).

10 The preferred starch component is esterized starch, preferably starch acetate, having a degree of substitution of 0.5 - 3, preferably 1.0 - 3 and in particular 1.3 - 3.

15 The other important starch component of the invention is represented by an ether formed by starch and a hydroxy alkyl group, the hydroxy alkyl component of which is preferably derived from ethylene oxide or propylene oxide. The molecular substitution of such an etherized starch is ca 0.05 - 6, preferably 0.1 - 3, in particular 0.3 - 2.

20 As mentioned above, the starch component can be plasticized by blending it with a known softener, i.e. plasticizing agent. The composition according to the invention includes thus according to a preferred application in particular 0.01 - 50 wt-%, preferably ca 1-30 wt-% of plasticizer. Any known plasticizers can be applied, e.g. water, acetic glycerol esters, propylene glycol, dipropylene glycol, glycerol, citric acid alkyl esters and mixtures thereof.

25 When using hydroxy alkyl esters of starch for the starch component of the composition, a plasticizer does not necessarily have to be added to the composition, since this starch component is per se sufficiently easily moulded (internal plasticization).

30 Biodegradable polyesters can further be included in the compositions according to the invention. These can further improve the strength properties and the hydrophobic character of the composition. Polylactide, polycaprolactone and cellulose-based ester derivatives are examples of suitable polyesters. The compositions contain such

derivatives in particular 0.01 - 30 wt-%, preferably ca 5 - 30 %. Cellulose acetate, cellulose propionate or cellulose butyrate or mixtures or mixed esters thereof are particular examples of the cellulose derivatives.

5 In addition to polyesters, biodegradable poly(ester urethanes) can be added to the compositions. As examples of these, let us mention hydroxy acid based polyesters coupled to each other by di-isocyanate compounds, and starch polymers to which polyesters (e.g. hydroxy acid based polyesters) are grafted by di-isocyanate compounds. Such compounds have good strength properties and including them can increase the same 10 properties of the present compositions.

The compositions according to the invention comprise 1-95, preferably ca 5-45 wt-%, of a fibrous material, which strengthens the material and provides discontinuous interfaces, which enhance the absorption of water. The fibrous material or fibre agent is added to 15 the rest of the material at any stage, at latest during the manufacturing of the intermediate product or the product, however. Organic fibres, inorganic fibres and mixtures thereof are examples of biodegradable fibres applicable to the invention. Preferably the fibre agent comprises fibres of a lactic acid based polymer (e.g. polylactide fibres), cellulose pulp (e.g. pine pulp), cereal cellulose fibres (e.g. barley 20 bark pulp), cereal pentosan (e.g. barley bark pentosan), cotton fibres, Abaca hemp fibres, sisal fibres, ramie fibres, flax fibres, jute fibres or biodegradable glass fibres. Out of the organic fibre materials, the cellulose fibres improve the impact strength values by ca 10 - 100 % (compared to a nonconsolidated composition), other plant based fibres by ca 50 - 150 % and the hydroxy acid polymer fibres by ca 200 - 600 %. The 25 compositions containing biodegradable glass fibres show impact strength values improved by ca 200 - 300 %.

Preferred compositions are listed in the following:

30 A composition comprising
- 40 - 90 wt-% starch acetate,

- 5 - 30 wt-% cellulose pulp
- 5 - 30 wt-% plasticizer and
- optionally 1 - 30 wt-% cellulose acetate

5 A composition comprising

- 40 - 95 wt-% hydroxy propyl starch,
- 5 - 30 wt-% cellulose pulp,
- 0 - 30 wt-% plasticizer and
- optionally 1 - 30 wt-% cellulose acetate

10

The present compositions can be prepared according to a method known per se by mixing the components of the composition, i.e., the starch based component, the optional cellulose derivative and the fibre agent, with each other. Preferably the starch component and the optional cellulose derivative are first melted.

15

In the new method according to the invention, designed for the preparation of starch acetate based compositions, the compositions are produced by esterizing the starch together with the plasticizer. Optionally, suitable esterizable cellulose material, such as chemical or mechanical cellulose pulp, can be added to the reaction blend, producing a mixture of plasticized starch acetate and cellulose acetate. As esterification agent, e.g. 20 acetic anhydride can be used, and as plasticizer any substance mentioned above, such as glycerol or acetic acid glycerol ester. The composition is then mixed with a biodegradable fibre agent in order to obtain a composition having a discontinuous microstructure.

25

When the weight share of the starch derivative is above 0.5 the invention provides a composition, in which the starch acetate forms a continuous phase.

The starch compositions according to the invention are plastic and melt-processible. 30 Typically the viscosity of the melt polymer is 10 - 5,000 Pa s, preferably 50 - 2,000 Pa s, measured with capillary rheometry at a temperature in the range of 140 to 200 °C

and at a shear rate of 200 1/s. The present starch compositions can be mixed with other polymers, e.g., by melt blending, in order to produce polymer mixtures. Plasticizers and filling agents, known per se, can further be added to the mixtures. Suitable filling agents are starch and modified starch components.

5

Semi-manufactured and final products can be manufactured from the compositions according to the invention. The products can be solid or at least partly hollow. Films and boards are examples of the products. The compositions can also be used for the coating of paper and cardboard, however. They can be used to produce specimens by injection moulding and products by compression moulding, thermoforming and blow moulding, such as packages, bags, sacks and bottles. Tooth mugs, flower pots and cocktail sticks are examples of special applications.

10 The compositions according to the invention have excellent properties of biodegradability; in particular the invention makes it possible to speed up the crumbling of products based on starch derivatives. This phenomenon will be examined in more detail in the following.

15 It is known that the biodegrading of starch derivative polymers in principle takes place in three phases: the phase of decreasing strength, the crumbling phase and the phase of return to circulation in Nature.

20 In the first phase, in which the products as such, or precrushed (in the following the "specimens"), are subjected to biodegrading conditions (e.g., composted, buried in the soil, or sunk in water), the products begin to adsorb water and various microorganisms begin to attach on their surfaces (e.g., bacteria, yeast, fungi, etc.). The strength of the products begins to weaken under the impact of the adsorbed water and the micro-organisms. The specimens retain their uniform form, until their strength reaches zero and/or the microorganisms have by their life functions corroded the specimens sufficiently. The phase of decreasing strength ends with that the specimen begins to disintegrate by the formation of fractures and crumbling.

In the crumbling phase fractures, cavities and increasing corrosion begin to form in the specimen, which has lost its strength, and following this the specimen begins to crumble to particles. This is preferred and important for the composting. In particular, with respect to composting, it is preferred that the specimens crumble as quickly as possible

5 into small pieces (having a maximum particle size (diameter) of ca 5 mm) after being mixed into the compost. Likewise it is preferred, that a specimen buried in the ground or sunk in water would crumble as quickly as possible after entering said environment.

10 Quick crumbling is preferred, because the crumbled material enters the third phase of biodegrading, i.e. the phase of return to circulation in Nature.

In the phase of return to natural circulation the small pieces (particles) of the crumbled specimen become part of the compost, soil humus, particles floating in water or bottom sediment. If the particles are biologically adaptable to the environment (i.e., do not

15 release toxic elements as they decompose further), the specimens can be considered to have returned to natural circulation when they have crumbled into small parts. Because the crumbling dramatically increases the surface of the materials, the decomposing effect of the micro-organisms increase strongly after crumbling, whereby the crumbling extends to smaller and smaller particles at the same time as low molecular decomposition

20 products dissolve from the particles for the micro-organisms to feed on. Part of the very small particles (typically less than 10 μm in diameter) can also be transported into the micro-organisms and become metabolized there. The most preferred result is that the original material returns in all to natural circulation, in which various particulate decomposition products can be further decomposed at their specific speed in the same

25 way as particles derived from nature also decompose in natural humus.

The crumbling of specimens has a particularly high significance for composting, since slowly crumbling specimens can slow down the handling and function of the compost. This is the case especially for industrial composters, in which the compostable material

30 should crumble as quickly as possible. Starch derivatives are hydrophobic, so they adsorb water relatively slowly. Also the surface corroding effect of the micro-organisms

is slower for these derivatives than for, e.g., thermoplastic starch. Thus, there has been a need to quicken the crumbling of the manufactured products in biodegrading circumstances, such as in composting.

5 In this invention it has surprisingly been found that the crumbling of the manufactured product in biodegrading circumstances can be significantly improved through providing discontinuous interfaces, which enhance the absorption of water, by mixing biodegradable fibres into the material at latest during the manufacturing of the intermediate product (semi-manufacture) or product.

10

Without confining to any specific model or mechanism, it can be noted that the effect of the biodegradable fibres on the quickening of the crumbling of the starch derivative products, seems to be based on the fact that the fibres provide discontinuous interfaces in the internal structure of the material, along which the absorption of water happens more easily and more quickly. The fibres and the interfaces of the material surrounding them, function as channels that make it possible for humidity external to the product to diffuse into the material. The water that is absorbed into the material, makes the material swell and loosens the fibres and the surrounding material from each other. As a result of these changes the material strength weakens faster than the strength of a material that do not contain fibres. Swelling of the material, weakening of the fibre-polymer interfaces and the decrease of the material strength, result in the formation of fractures and the crumbling of the material begins earlier and proceeds faster than the crumbling of a corresponding material without fibres. This fact is of a high practical significance, since products containing biodegradable products will thus crumble and return to natural circulation, in compost, soil or water, quicker than products that do not contain fibres.

25 The following examples will describe the invention in more detail. The degrees of substitution of the starch acetates as given in the examples are determined according to Wurzburg (Wurzburg, O.B., Acetylation, In: Methods in Carbohydrate Chemistry, Vol. IV, R.L. Whistler (Ed.), Academic Press, New York and London, 1964, p. 288). The molar masses are determined on the basis of GPC-analysis in the research laboratory of

Alko Group Ltd. Equipment HP-1090, two columns in a cascade (Waters, Ultra Hydrogel 2000), solvent 50 nM NaOH, temperature 40 °C, dextran standards, detectors RI and viscosity detectors. Molar mass is determined from the starch used as raw material.

5

Example 1

Preparation of starch acetate

10 Starch acetates having different degrees of substitution and molar masses were prepared by using the reagent amounts described in the following table:

Table 1. Preparation of starch acetate, reaction conditions and product analysis

15	Test no.	Starch quality	Amounts and reaction conditions				Product analysis	
			Amount of starch	Acetic anhydride	NaOH 50 %	Reaction time	Dry matter	D.S.
	1	Native barley starch.	40 kg	175 kg	4.4 kg	10 h	99.0 %	2.8
	2	"	34 kg	150 kg	3.8 kg	5 h	91.4 %	1.7
	4	Enzym. hydrol. barley starch	38 kg	150 kg	8.3 kg	5 h	96.6 %	2.84
20	5	Acid hydrol. barley starch	750 g	3000 g	165 g	5 h	98.8 %	2.9

a,b and c are barley starch qualities of different molar masses (Table 2)

25 The starch or barley flour and the acetic anhydride were charged into a reactor and the agitation was turned on. The temperature of the mixture was raised to 60 °C and an 50 % aqueous sodium hydroxide solution was gradually added. The temperature of the reaction mixture increased by about 40 - 60 °C during the addition. After the addition of

NaOH the temperature of the reaction mixture was raised to 125 °C for the time period indicated in the table. After the reaction the mixture was cooled and precipitated by adding an about 5-fold amount of water under vigorous agitation. The precipitate was filtered and washed with water until the pH of the washing water was > 5. The 5 precipitate was spray-dried.

The relative differences between the molar masses of the starches used from acetate preparation have been characterized by Brabender-viscosity measurements. The 10 determinations were carried out by using Brabender-viscoamylography. The instrument measures the momentum needed for balancing the viscosity increase of the starch slurry during a programmed heating cycle. The process is widely used in the starch industry for illustrating gelatinization of various starches and the properties of the formed pasta. A decrease of the molar mass will show as a lowering of the viscosity.

15 The results are given in the following Table 2:

Table 2. Brabender-viscosities and temperatures illustrating gelatinization of the starches used for preparing starch acetates

5	Starch quality	Temperature at the outset of gelat. °C	Temperature at maximum viscosity °C	Brabender-viscosity ¹				
				B1 (BU)	C (BU)	D (BU)	E (BU)	F (BU)
10	Native barley starch ^a	61.1	89.6	2760	2332	1715	10	2445
15	Enzym. hydrol. barley starch. ^c	30.8	30.8	231	62	31	211	64
	Acid hydrol. barley starch ^b	30.4	71.3	4	20	0	0	21

¹ Conditions of measuring the Brabender-viscosities:

- Starch content of aqueous slurry 12 %
- Heating cycle: Initial temperature 30 °C, increase of temperature to 95 °C at a rate of 1.5 °C/min and a temperature hold at 95 °C for 15 min, decrease of temperature to 55 °C at a rate of 1.5 °C/min and a temperature hold at 55 °C for 10 min.
- Rotation speed: 75 1/min
- Measurement area: 700 cm²
- Abbreviations:
 - B1 = Momentum at maximum viscosity
 - C = Momentum when the temperature had reached 95 °C
 - D = Momentum at the outset of the cooling cycle
 - E = Momentum when the temperature had reached 55 °C
 - F = Momentum at the end of the measurement
 - BU = Brabender unit

Example 2**Preparation of plasticized starch acetate**

Plasticized starch acetate was prepared from the following reagents:

5

Table 3. Reagents used in the preparation of plasticized starch acetate

Reagent	Product 2 a	Product 2b
Ohrakas*	60 g	-
Thermoplastic starch acetate, DS 0.3**	-	100 g
Glycerol	40 g	-
Acetic acid anhydride	250 g	250 g
NaOH, 50 %	22 g	22 g

15

* Native barley starch, manufactured by Primalco. Nurmijärvi

** Thermoplastic starch acetate is a starch acetate having a low degree of substitution, which has been preplasticized by melt agitating at a temperature of 140°C with water and glycerol (water 60 g, glycerol 60 g and 100 g starch acetate DS 0.3) for 14 min., whereby almost all water evaporated. Thermoplastic starch contains ca 40% glycerol.

20 Starch, glycerol and acetic acid anhydride were charged into the reactor under agitation. (The thermoplastic starch already contained the desired amount of glycerol.) The temperature of the blend was raised to 45 °C and an 50 % aqueous NaOH solution was gradually added. After the addition of sodium hydroxide the temperature of the reaction mixture was raised to 125 °C for 5 hours. The water that was formed during the reaction (and the acetic acid that might have been distilled) was collected with a water separator. The acetic acid and the acetic acid anhydride that might not have reacted was distilled from the reaction mixture under slight vacuum, cautiously so as not the acetic acid 25 glycerol esters would yet be distilled. The temperature of the distillate was 38-42 °C and

30

the pressure 80-100 mmHg. After the distillation the rest of the acetic acid (smell) was removed by nitrogen stripping.

The acetyl contents of the thus prepared thermoplastic starches were 2a: 30 % and 2b: 5 38 %.

Example 3

Preparation of cellulose starch acetate

10 Three different modifications of cellulose and starch by using the amounts of reagents given in following Table 4.

Table 4. Amounts of reagents used in the preparation of cellulose starch acetates

15	Test	Starch (g)	Acetic anhydride (g)	50 % NaOH	Cellulose (g)
	1	100	400	15	40
	2	100	400	15	40
	3	100	700	15	40

20

Test 1

25 Starch and acetic anhydride were charged into a retort equipped with a motor agitator, refluxer, dropping funnel and a thermometer. The agitation was turned on and the temperature of the mixture was raised to 45 °C. An 50 % aqueous sodium hydroxide solution was cautiously dropped into the mixture. The temperature of the reaction mixture increased by about 40 - 60 °C during the addition. When all the NaOH had been added, the temperature of the reaction mixture was raised to 125 °C for 5 hours. After the reaction the mixture was cooled and precipitated from pulp slurry. The pulp slurry 30 was prepared from 40 g dry cellulose chaff cut from a pulp sheet by slurring and

homogenizing with UltraTurrax in 5 litres of water. The precipitate was filtered and washed with plenty of water until pH > 5. The precipitate was dried at room temperature.

5 Test 2

The reaction was performed according to the method described in Test 1. After a reaction time of five hours, 40 g dry cellulose chaff cut from a pulp sheet was added to the reaction mixture, which was left for homogenization for 10 minutes. The mixture 10 was precipitated from water and the precipitate was filtered, washed with plenty of water and air-dried at room temperature.

Test 3

15 Starch, acetic anhydride and 40 g dry cellulose chaff cut from a pulp sheet was added to the reaction equipment described in Test 1. Starch and cellulose was left to react for five hours at 125°C. After the reaction the mixture was precipitated from water, filtered and washed with plenty of water and air-dried.

20 The analysis of the products obtained in Tests 1,2 and 3 are presented in Table 5.

Table 5. Analysis of cellulose starch acetates

Test	Degree of substitution, DS	Dry matter (%)	Ash (%)	Molar mass of reagent starch (g/mol)
25	1	2.15	98.5	$M_w=117,300$ $M_w=32,170$
	2	2.31	98.7	"
	3	1.63	98.1	"

Example 4

Preparation of a starch acetate cellulose fibre composition

5 The following composition (composition A) was prepared, comprising:

- 70 % by weight of enzymatically hydrolyzed starch acetate having a degree of substitution 2.84, and
- 30 % by weight of glycerol triacetate, manufactured under the brand name Priacetin 1580 (Unichema International)

10 The mixture was plasticized and mixed in Brabender Plasti-Corder^R PL2000 W350E-measuring mixer. The mixing process was carried out under the following conditions:

Temperatures: 160 °C/160 °C (2 zones)

15 Speed of the blades: 52 rpm

Mixing time: 10 minutes

20 The thus mixed composition was then processed by a SP2-piston injection moulding machine into specimens suitable for the Charpy impact strength test. Moulding temperature was 160°C.

Impact strength was determined by International Standard SFS-ISO 179. The test specimens were of type ISO 179/2D (unnotched). Before testing the test specimens were stored in a closed plastic bag. The impact strength of the test specimens thus obtained 25 was 2.8 kJ/m².

The following composition (composition B) was prepared, comprising:

- 60 % by weight of enzymatically hydrolyzed starch acetate having a degree of substitution was 2.84 (same as in composition A)
- 10 % by weight of pine cellulose fibres
- 30 % by weight of glycerol triacetate, manufactured under the brand name

Priacetin 1580 (Unichema International; same as in composition A)

The same processing conditions and impact strength testing methods were used as for the composition A. The impact strength of the test specimens was 4.1 kJ/m².

5

The proportional impact strength was determined as follows:

$$\begin{aligned}\text{Relative strength} &= \text{Strength of Composition B} / \text{Strength of Composition A} \\ &= 4.1 \text{ kJ/m}^2 / 2.8 \text{ kJ/m}^2 = 1.5\end{aligned}$$

10

The impact strength of the composition could be enhanced by increasing the amount of cellulose fibres (shown in Table 6).

15

Table 6. Relative impact strength values of the starch acetate cellulose fibre compositions

20

25

Composition	Relative impact strength
* 70 wt-% starch acetate (DS 2.84)	1.0
* 30 wt-% glycerol triacetate	
* 60 wt-% starch acetate (DS 2.84)	1.5
* 10 wt-% pine cellulose fibres	
* 30 wt-% glycerol triacetate	
* 55 wt-% starch acetate (DS 2.84)	1.9
* 15 wt-% pine cellulose fibres	
* 30 wt-% glycerol triacetate	
* 50 wt-% starch acetate (DS 2.84)	3.3
* 20 wt-% pine cellulose fibres	
* 30 wt-% glycerol triacetate	

Example of comparison

A mixture according to Example 1 of the patent WO 95/04106 was prepared and tested according to Example 4 above. The mixture comprised the following materials:

5 - starch 11.5 kg (of this 35 wt-% was plasticizer, sorbitol)
 - ramie (or optionally sisal) 840 g (fibre length 0.5 mm)
 - stearic acid 200 g

The ratio of starch/ramie/stearic acid was 91.7 / 6.7 / 1.6. A corresponding mixture was also prepared from starch acetate (DS 2.8), which was plasticized with glycerol triacetate. Sisal was used for the fibre, with a fibre length of 3-4 mm.

10 The relative impact strength values of the compositions thus obtained are presented in Table 7.

15 **Table 7. Relative impact strength values of compositions of native starch and of starch acetate**

Composition	Relative impact strength
* 91.7 wt-% native starch (out of which 35 wt-% sorbitol) * 6.7 wt-% sisal * 1.6 wt-% stearic acid	1.0
* 91.7 wt-% starch acetate (out of which 35 wt-% glycerol triacetate) * 6.7 wt-% sisal * 1.6 wt-% stearic acid	4.0

Example 5

Compositions comprising various biodegradable fibres

30 Starch based compositions were prepared as in Example 4 (composition B) with different

biodegradable fibre materials. The processing conditions and testing methods were the same as in Example 4.

The following compositions were produced:

5 - 55 wt-% starch acetate (DS 2.84)
- 30 wt-% glycerol triacetate
- 15 wt-% various biodegradable fibres

The relative impact strength values of the compositions thus obtained are given in Table
10 8.

**Table 8. Relative impact strength values of compositions containing various
biodegradable fibres**

	Biodegradable fibre material	Relative impact strength
15	PLA-fibres	4.0
	Pine cellulose	1.9
	Barley bark cellulose	1.3
	Barley bark pentosan	1.1
	Cotton	1.4
	Abaca hemp	2.4
	Sisal	1.9
	Ramie	2.2
	Flax	2.7
	Jute	2.2
25	Biodegradable glass	2.5

Example 6

Compositions comprising starch acetate, glycerol triacetate and pine cellulose

5 Compositions comprising native starch acetate (DS 2.8), various amounts of glycerol triacetate and pine cellulose fibres were prepared and tested as in Example 4. The relative strength values of the thus obtained compositions are given in Table 9.

Table 9. Relative impact strength values of compositions comprising native starch acetate, glycerol triacetate and pine cellulose fibres

10

Composition	Relative impact strength
* 63 wt-% starch acetate (DS 2.8)	1.0
* 22 wt-% glycerol triacetate	
* 15 wt-% pine cellulose fibres	
* 60 wt-% starch acetate (DS 2.8)	1.1
* 25 wt-% glycerol triacetate	
* 15 wt-% pine cellulose fibres	
* 57 wt-% starch acetate (DS 2.8)	1.5
* 28 wt-% glycerol triacetate	
* 15 wt-% pine cellulose fibres	
* 55 wt-% starch acetate (DS 2.8)	2.9
* 30 wt-% glycerol triacetate	
* 15 wt-% pine cellulose fibres	

25

Example 7

Compositions comprising starch acetate, cellulose acetate and cellulose fibres

Cellulose acetate and cellulose fibres were mixed with starch acetate as in Example 4. 30 The impact strength of the compositions was determined as in Example 4.

The relative impact strength values of the thus obtained compositions are given in Table 10.

Table 10. Relative impact strength values of compositions comprising starch acetate, cellulose acetate and cellulose fibres

	Composition	Relative impact strength
5	<ul style="list-style-type: none"> * 70 wt-% enzymatically hydrolyzed starch acetate (DS 2.84) * 30 wt-% glycerol triacetate 	1.0
10	<ul style="list-style-type: none"> * 50 wt-% enzymatically hydrolyzed starch acetate (DS 2.84) * 30 wt-% glycerol triacetate * 15 wt-% cellulose acetate (Aldrich) * 5 wt-% pine cellulose fibres 	5.8
15	<ul style="list-style-type: none"> * 50 wt-% enzymatically hydrolyzed starch acetate (DS 2.84) * 30 wt-% glycerol diacetate * 10 wt-% cellulose acetate (Aldrich) * 10 wt-% pine cellulose fibres 	2.5

20

Example 8

Compositions based on hydroxy propyl starch

Compositions containing hydroxy propyl starch (COHPOL DL 20, Primalco Ltd, 25 Polymer unit (MS 1.44) and/or glycerol and/or pine cellulose pulp fibres were prepared according to Example 4. The flexural strength and fixed elasticity modulus of the compositions were determined according to the standard ASTM D790M-86. The influence of the plasticizer and the cellulose fibres on the mechanical properties of hydroxy propyl starch were determined on basis of the impact strength, flexural strength and fixed elasticity modulus (Table 11). The elasticity modulus was determined only if 30 the hydroxy propyl starch (HPS) clearly was elastic at room temperature.

Table 11. The properties of compositions containing hydroxy propyl starch

Composition	Relative impact strength	Relative flexural strength	Relative elasticity modulus
* 100 wt-% HPS	1.0	1.0	
5 * 80 wt-% HPS * 20 wt-% cellulosic fibres	2.7	3.4	
10 * 94 wt-% HPS * 6 wt-% glycerol	1.2	0.9	
15 * 74 wt-% HPS * 20 wt-% cellulosic fibres * 6 wt-% glycerol	3.8	3.5	
20 * 88 wt-% HPS * 12 wt-% glycerol	1.4	0.1	1.0
* 68 wt-% HPS * 20 wt-% cellulosic fibres * 12 wt-% glycerol	7.3	0.9	13.2
* 58 wt-% HPS * 30 wt-% cellulosic fibres * 12 wt-% glycerol	10.4	1.8	31.3

25

Example 9**Preparation of injection moulded articles**

30 The following compositions (compositions I and II) were prepared and they were plasticized and blended as described in Example 4:

I - 75 wt-% native starch acetate (DS 1.7)
 - 25 wt-% glycerol triacetate

II

- 60 wt-% native starch acetate (DS 1.7)
- 25 wt-% glycerol triacetate
- 15 wt-% pine cellulose pulp fibres

5 The thus obtained mixtures were crushed and injection moulded in an injection moulding machine, Engel 75, to form cup-shaped articles. The moulding temperature was 180 °C. The volume of the cup was about 0.25 dm³, its weight was 50 g and the wall thickness about 2 mm.

10 A drop test was performed. 10 cups of each composition (I and II, respectively) were dropped on a stone floor from a height of 1 m.

All cups of composition I were broken down to small pieces. Not one of the cups prepared from composition II got any visible damages.

15 Further, by using the method of Example 4, a composition III was prepared for the purpose of comparing the product properties.

III - 53 wt-% native starch acetate (DS 1.7)

20 - 10 wt-% commercial cellulose acetate (Dexel)

- 15 wt-% pine cellulose pulp fibres
- 22 wt-% glycerol triacetate

Example 10

25 Mixture of starch acetate/triacetin/calcium metaphosphate

Biodegradable glass fibres were prepared from calcium metaphosphate powder by melting it in a platinum crucible. The molten glass was drawn through a hole in the bottom of the crucible to form a fibre at a temperature of 1150 °C. The diameter of the fibre was about 10 30 µm and it was adjusted by regulating the drawing rate of the fibre. The fibres were assessed by drawing them through a dilute starch solution and reeling them on a bobbin. The

flexural strength of the fibres was about 300 MPa and flexural modulus 25 GPa.

Preparation of composite material: A slightly twisted roving, consisting of ca 100 bioglass fibres, was drawn through the crosshead nozzle of the extruder at the same time as the 5 crosshead nozzle was fed by the extruder with melt composition I according to Example 9. The bundle of fibres was impregnated with the polymer melt in the crosshead nozzle and a cylindrical composite parison (ca 0.2 mm in diameter) was drawn from the nozzle. The parison was cut in pieces of 7 cm length, and the pieces were compressed in a cylindrical compression mould into sticks with a cylindrical cross section, having a diameter of 2 mm 10 and length of 6 cm. The flexural strength obtained for the sticks with three-point bending was 40 MPa. The flexural strength was 20 MPa for corresponding unconsolidated sticks, prepared from starch derivative by injection moulding (Composition I, Example 9).

Example 11

15 Compositions based upon grafted starch

Compositions were prepared from the grafted starch material described in Patent Application PCT/FI95/00148 (Example 6) containing 10 and 20 wt-% pine cellulose pulp 20 fibres. The conditions of Example 4 were maintained during blending. The impact strengths of the obtained compositions were also determined according to the test method presented in Example 4.

The relative impact strength values of the thus obtained compositions are given in Table 12.

25 The impact strength of the grafted starch derivative can be improved by increasing the amount of cellulosic fibres in the composition.

Table 12. The relative impact strength values of compositions containing grafted starch derivatives and cellulosic fibres

Composition	Relative impact strength
* Grafted starch derivative (material according to PCT/FI95/00148)	1.0
* 90 wt-% grafted starch derivative	2.6
* 10 wt-% pine cellulose pulp fibres	
* 80 wt-% grafted starch derivative	3.9
* 20 wt-% pine cellulose pulp fibres	

In the following Examples, the product properties of the biodegradable starch composition according to the invention are examined.

15

Example 12

Preparation of a sheet from cellulosic fibres/starch acetate by compression moulding

A starch acetate/triacetin mixture plastisized according Example 9 was prepared using the components at the weight ratio 75/25. The degree of substitution of the starch acetate was 2.9.

25

The plasticized mass was cooled in liquid nitrogen and pulverized. The pulverized mass was filtered and the fraction below 0.25 mm was used in the compression moulding. The mixture of cellulose fibre and plasticized starch acetate was premixed in a vessel in the ratios 90/10 (mixture A) and 70/30 (mixture B). The thus prepared mixture was charged evenly in a compression mould with a diameter of 98 mm. The thickness of the sheets produced was ca 1.5 mm. For comparison the corresponding board was prepared also out of sole cellulose fibre. The temperature of compression moulding was 150 °C, the time of compression 5 minutes and the force 100 kN. The mould was cooled to a

temperature of ca 80°C, after which the mould was opened and the compression moulded board was removed from the mould.

From the compression moulded boards, test sticks were cut with the dimensions 5 15x1.5x60 mm. The sticks were stored in closed plastic bags between preparation and testing. For the test sticks the flexural strength was determined by three-point bending in a test adapted to the standard ASTM D 790-86. The results are given as relative values in Table 11 determined as in Example 3 for the pure cellulose fibre as compared to the compression moulded test sticks.

10

Table 13. Relative flexural strength values for compression moulded specimens

Material	Relative flexural strength
Compression moulded cellulose fibre	1.0
Mixture A	1.3
Mixture B	3.4

Example 13

Water adsorption tests

20

Water adsorption determinations for the biodegradable starch composition were made at VTT Biotechnology and Food Research. The samples were balanced in a chamber, the humidity of which had been regulated with saturated salt solutions. The salts LiCl, Mg(NO₃)₂, NaCl, (NH₄)₂SO₄, KNO₃ and K₂SO₄ were used. The relative humidity values 25 were 12, 33, 56, 77, 91 and 97 %. The chamber was kept at 20 °C and the mass of adsorbed water was determined gravimetrically after 7 days.

30 The samples examined were starch acetates prepared as in Example 1, compositions II and III prepared as in Example 9, native barley starch and glycerol triacetate. The results of the water adsorption determination are given in Table 14.

Table 14. Water adsorption by starch, starch acetates, cellulose fibre, glycerol triacetate and fibre containing starch acetate compositions

Material	Change of mass (in %) for varying humidity						
	0 %	12 %	33 %	56 %	77 %	91 %	97 %
5 Native barley starch powder	0	9	10	14	16	25	34
Starch acetate powder Example 1/ Test 1	0	0	0	0	1	1.5	4
10 Starch acetate powder Example 1/ Test 3	0	0	0.6	1.5	2.5	5.4	5.7
Pulp fibre	0	0	1	3.3	5.7	12	14
Glycerol triacetate	0	0.5	0.6	1	1.5	2.7	3
15 Composition II / Ex. 9 (Granulate)	0	0	0	1.0	2.3	6.5	10.5
Composition III/ Ex. 9 (Granulate)	0	0	0	1	1.5	6	9.8

20 The results show that the starch acetates clearly adsorb less water than native barley starch. For high water contents the granular compositions II and III adsorbed a little less water than pure pulp fibre, but clearly more than glycerol triacetate and the starch acetates of Tests 1 and 3 in Example 1.

Example 14

25 Migration tests

30 The total amount of elements that might migrate from the biodegradable starch compositions into foodstuffs, the so called total migration, was determined in the Laboratory of Bio- and Food Technology of the Technical Research Institute. The method that was used is described in the European prestandard ENV 1186-3 "Materials and Articles in Contact with Foodstuffs; Plastics-Test Methods for Overall Migration

into Aqueous Food Simulants by Total Immersion". The determination is gravimetrical: the sample is immersed totally into the solution that emulates foodstuff, the simulant. Distilled water, 3 % acetic acid and 15 % ethanol (decision 262/92 of the Ministry of Trade and Industry, directive 85/572/EEC) were used as simulants. The test was 5 performed in conditions according to the decision 261/92 of the Ministry of Trade and Industry, directive 82/711/EEC: 24 hours in 40 °C. A smaller test surface was used than what is recommended in the European prestandard: 0.2 dm² instead of 1 dm².

10 Table 15 presents the migration into foodstuffs of the compositions I, II and III as described in Example 9.

Table 15. Total migration of biodegradable starch compositions (mg/dm²) into water, 3 % acetic acid and 15 % ethanol during 24 hours at 40 °C.

15	Sample	Distilled water	3 % acetic acid	15 % ethanol
	Composition I	1.0	3.0	5.5
	Composition II	0.7	1.5	0.8
	Composition III	0.5	2.5	2.5

20

On the basis of the results, it can be noted that all tested samples are suited for short-term contact with moist, neutral, acid and alcoholic foodstuffs (10 mg/^{DM} is the maximum allowable migration according to the decision 397/94 of the ministry of Trade 25 and Industry). Furthermore the results show that less migration occurs from the starch composition II, which contains fibre, than from the starch composition I without fibre.

Example 15**Biodegradability/compostability**

5 The biodegradability of the starch compositions was tested with the Head-Space test developed at VTT Biotechnology and Food Research. The samples were weighed (15 g) into head-space bottles, into which was added 50 ml mineral salt solution and microbe graft prepared from compost in the thermophile stage. The sample bottles were incubated in water-bath at + 55 °C and the biodegradability was determined based on the carbon dioxide that was formed.

10

10 The biodegradability of the compositions II and III described in Example 9 was examined as a function of time. The biodegradability was determined as the ratio of the carbon dioxide that actually was released from the sample to the amount that theoretically could be released. The results showed that after 28 days 46 % more carbon dioxide had been released from the starch composition II and 25 % more from the composition III than from starch acetate as such.

Claims:

1. A melt-processible, compostable starch composition, characterized in that
 - a) the composition contains
 - 5 to 99 wt-% of a plasticized starch derivative and
 - 1 to 95 wt-% of a biodegradable fibrous material,
 - b) the microstructure of the composition is discontinuous and formed by a starch derivative phase and a fibrous material phase and porosity, if any.
- 10 2. The composition according to claim 1, wherein the impact strength of the composition is at least 10 % better than that of the plasticized starch derivative.
- 15 3. The composition according to claim 1 or 2, wherein the composition contains about 30 to 95 wt-% of the plasticized starch derivative and 5 to 70 wt-% of the biodegradable fibrous material.
- 20 4. The composition according to any one of claim 1 to 3, wherein the composition contains at least 50 wt-% of the plasticized starch derivative, which forms the continuous phase of the composition, the fibrous material phase forming discontinuous interphases which enhance biodegrading of the composition.
- 25 5. The composition according to any one of claims 1 to 4, wherein the plasticized starch component is selected from the group consisting of starch derivatives prepared by oxidation, esterified starch derivatives, etherified starch derivatives, grafted starch derivatives, cross-linked starch derivatives, hydroxy alkylated starch derivatives and/or cationic starch derivatives, the raw material of the starch derivatives being a native or enzymatically or chemically hydrolyzed starch having an amylose content of 0 to 100 % and an amylopectine content of 100 to 0 %.
- 30 6. The composition according to claim 5, wherein the starch-based component is derived from an ester of starch and one or more aliphatic C₂₋₂₄ carboxylic acids.

7. The composition according to claim 6, wherein the carboxylic acid component of the ester is derived from acetic acid, propionic acid or butyric acid or a mixture thereof.
- 5 8. The composition according to claim 6, wherein the carboxylic acid component of the ester is derived from a naturally occurring saturated or unsaturated fatty acid.
9. The composition according to claim 8, wherein the carboxylic acid component is derived from palmitinic acid, stearic acid or a mixture thereof.
- 10 10. The composition according to any one of claims 6 to 9, wherein the starch-based component contains both long- and short-chained carboxylic acid components.
11. The composition according to claim 10, wherein the starch component is a mixed ester of starch and acetic acid and stearic acid.
- 15 12. The composition according to any one of claims 5 to 9, wherein the degree of substitution of the esterified starch is 0.5 to 3, preferably 1 to 3, in particular 1.5 to 3.
- 20 13. The composition according of any one of the preceding claims, wherein the starch-based component is derived from an ether formed by starch and a hydroxy alkyl group.
14. The composition according to any one of the preceding claims, wherein the hydroxy alkyl component of the ether is derived from ethylene oxide or propylene oxide.
- 25 15. The composition according to any one of the preceding claims, wherein the molar substitution of the etherified starch is about 0.05 to 6, preferably 0.1 to 3, in particular 0.3 to 2.
- 30 16. The composition according to any one of the preceding claims, wherein the composition further contains 0.01 to 50 wt-%, preferably about 1 to 30 wt-% of a plasticizer.

17. The composition according to claim 16, wherein the plasticizer comprises water, glycerol esters of acetic acid, propylene glycol, dipropylene glycol, glycerol, alkyl esters of citric acid and/or mixtures thereof.
- 5 18. The composition according to any one of claims 1 to 17, wherein it further contains 0.01 to 30 wt-%, preferably about 5 to 30 wt-% of a biodegradable polyester, such as polylactide, polycaprolactone or a cellulose ester, such as cellulose acetate, propionate or butyrate or mixtures thereof or mixed esters thereof.
- 10 19. The composition according to any one of the preceding claims, wherein it contains 5 to 45 wt-% fibrous matter.
- 15 20. The composition according to any one of the preceding claims, wherein the dry matter of the composition is formed by fibres of a lactic acid polymer, by cellulose pulp, by cereal cellulose fibres, cereal pentosan, cotton fibres, fibres of Abaca hemp, sisal fibres, ramie fibres, flax fibres, jute fibres or biologically degradable glass fibres.
- 20 21. The composition according to claim 1, wherein it contains 40 to 90 wt-% starch acetate, 5 to 30 wt-% cellulose pulp and 5 to 30 wt-% plastisizing agent.
- 25 22. The composition according to claim 1, wherein it contains 40 to 95 wt-% hydroxy propyl starch, 5 to 30 wt-% cellulose pulp and 0 to 30 wt-% plastisizing agent.
23. The composition according to claim 21 or 22, wherein it further contains 1 to 30 wt-% cellulose acetate.
- 30 24. A polymer blend, characterized in that it contains a polymer composition according to claim 1 mixed with a thermoplastic.
25. The polymer composition according to claim 1 or the polymer blend according to claim 24 mixed with plastisizers and/or fillers.

26. The polymer composition according to claim 1 or the polymer blend according to claim 24, wherein the filler used comprises starch or modified starch.

5 27. The use of a polymer composition according to any one of claims 1 to 23 for preparation of films or sheets.

10 28. The use of a polymer composition according to any one of claims 1 to 23 for preparation of injection moulded articles and for preparation of thermoformed and blow moulded articles such as packages, bags, sacs and bottles.

15 29. The use of a polymer composition according to any one of claims 1 to 23 for coating of paper or cardboard.

30. The use of a polymer composition according to any one of claims 1 to 23 for preparation of articles made by compression moulding.

20 31. A process for preparing a compostable starch composition, wherein native starch is esterified in order to produce a plastisized starch derivative, characterized by

- esterifying the starch together with glycerol to produce a mixture containing starch acetate and a glycerol ester of acetic acid, and
- blending said mixture with a biodegradable fibrous material to produce a composition having a discontinuous microstructure.

25 32. The process according to claim 31, which comprises preparing a composition wherein starch acetate forms the continuous phase.

33. The process according to claim 31 or 32, wherein starch and glycerol are esterified with acetic anhydride.

30 34. The process according to any one of claims 31 to 33, wherein cellulose pulp is added to a mixture of starch and glycerol before the esterification, whereby a plastisized mixture

is obtained after the reaction, which contains a starch ester, a glycerol ester of acetic acid and a cellulose ester.

35. The process according to claim 34, wherein pine pulp is used as cellulose pulp.

5

36. A process for preparing a compostable starch composition, wherein native starch is esterified in order to produce a plastisized starch derivative, characterized by

- esterifying starch together with cellulose pulp and glycerol to produce a plastisized mixture containing starch acetate, cellulose acetate and a glycerol ester of acetic acid, and
- blending said mixture with a biodegradable fibrous material to produce a composition having a discontinuous microstructure.

10

37. The process according to claim 36, which comprises preparing a composition wherein the plastisized starch acetate forms the continuous phase.

15

38. The process according to claim 36 or 37, wherein the starch, the cellulose pulp and the glycerol are esterified with acetic anhydride.

20

39. A method for improving the crumbling rate of intermediate products and/or articles made from starch derivatives during biodegradation, characterized by producing within the infrastructure of the material discontinuity interfaces, which improve water absorption, by mixing biodegradable fibers into the material at the latest during the manufacture of the intermediate product or the article.

25

40. The intermediate product and/or article according to claim 39, wherein the biodegradable fibers are organic fibres, inorganic fibres or mixtures thereof.

30

41. The continuous or discontinuous, massive or partly onto article according to claim

40.

INTERNATIONAL SEARCH REPORT

International application No. PCT/FI 96/00403

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08L 3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPDOC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9504106 A1 (BIOTEC BIOLOGISCHE NATURVERPACKUNGEN GMBH), 9 February 1995 (09.02.95), abstract, page 1, 2nd paragraph, page 4, 3rd paragraph, line 1 - line 11, claim 10, 11 --	1,4,18, 20-21,23,25
A	WO 9427796 A1 (BIOTEC BIOLOGISCHE NATURVERPACKUNGEN GMBH & CO. FORSCHUNGS- UND ENTWICKLUNGS KG), 8 December 1994 (08.12.94), claims 1-4, abstract -- -----	1,20,27,30

 Further documents are listed in the continuation of Box C. See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

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Date of mailing of the international search report

09-10-1996

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INTERNATIONAL SEARCH REPORT

Information on patent family members

05/09/96

International application No.

PCT/FI 96/00403

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A1- 9504106	09/02/95	AU-A-	7228894	28/02/95
		CA-A-	2168215	09/02/95
		EP-A-	0711324	15/05/96
WO-A1- 9427796	08/12/94	DE-A-	4317692	01/12/94
		EP-A-	0700329	13/03/96